A Computational Benchmarking Study of Reaction Barriers of Ir and Ru Photocatalysts Using DFT Functionals for Single-Electron Transfer Reactions

SYNOPSIS

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Synopsis of Research Work for Ph.D. Degree in the Faculty of Science(Chemistry)

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a) Purpose and Need of the Study

Photoredox catalyzing has quickly established itself as an efficient strategy for modern organic synthesis, it permits challenging bond formation through easy to light treatments under mild conditions, focusing on visible light. In such reactions a transition-metal photocatalyst (often an Iridium(III) or Ruthenium(II) polypyridyl complex) interacts with light, absorbing light and developing an excited state suitable for SET via organic catalysts. This SET process produces radical intermediates with further bond formation, creating novel reaction routes that cannot be accessed under standard thermal conditions. Examples of prototypical complexes such as fac-$Ir(ppy)_3$ (ppy = 2-phenylpyridine) and $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), consist of long-lived excited triplet states and high excited-state redox potentials and have been readily employed. Such photocatalysts can be mediated by reductive quenching (accepting an electron from a donor to form a reduced metal complex) or oxidative quenching (where the electron is donated to an acceptor to generate an oxidized complex) cycles. The main difficulty is that the SET event (frequently the rate- determining step) consists of the removal of an electron from the excited catalyst to the substrate, which determines the kinetics and selectivity of the reaction. The prediction of the activation barriers to these SET-induced steps can help to rationalize why some photoredox reactions are successful and contribute to design of new catalytic systems.

However, direct experimental measurement of activation free energies for these transient radical-forming steps is uncommon, thereby a critical need for an established theoretical tool to address this gap in knowledge. Computational chemistry with a focus on density functional theory (DFT) represents an inexpensive way to estimate reaction energetics and probe reactions in photoredox catalysis. Yet predicting activation barriers for outer-sphere electron transfer and following up radical reactions in precise fashion is still difficult.

Photoredox systems strain DFT to its limits: open-shell radical species, charged states, heavy transition metals (Ir, Ru), substantial solvent effects. There are various DFT exchange–correlation functionals which can produce completely different barrier heights for a given reaction. For instance, the widely used B3LYP functional, widely used in organometallic catalysis, may underestimate some barrier heights because of self-interaction error. Recent insights have suggested testing more advanced functionals (from range-separated hybrids to meta-GGAs or double-hybrids) for difficult catalytic reactions (e.g. Sperger et al., 2015). So far, the majority of computational studies of photoredox catalysis have concentrated on redox potentials (thermodynamic quantities), instead of activation free energies (kinetic quantities). There are gaps in the literature, and there is a lack for systematic comparison of DFT functionals as reference points for predictions of reaction barrier for Ir/Ru photoredox catalysis. This gap is at the root of the current work and serves the scientific quest for accurate computational methods for photoredox reaction kinetics. Through careful scrutiny of these multiple DFT functionals with known experimental data, or in a higher-level way we hope to elucidate the best and valid approaches for calculating SET reaction barriers. This will serve to confirm DFT as a predictive framework for photoredox catalysis and to provide chemists guidance in their selection of suitable functionals that will support mechanistic explorations in the future. In the end, this study will fill the critical gap for best practice recommendations on how to simulate these important light-driven reactions.

b) Details of the Project with Chapterization

Thesis Structuring: The dissertation has been organized as follows to meet the above goals and contain numerous chapters covering the various portions of the research. Below are theheadings of the entire chapter and the very brief part to it:

Chapter 1: Introduction – This chapter will present the study on photoredox catalysis and its importance in organic synthesis. It will outline how Iridium and Ruthenium polypyridyl complexes can function as visible light photocatalysts for single electron transfers towards the radical intermediates under mild conditions. It will define general concepts (photocatalyst excited states, reductive vs. oxidative quenching cycles) and

describe representative examples from literature. It will also articulate the original problem statement – the difficulty in predicting reaction kinetics for these systems – and put together the guiding question of how computational chemistry (DFT) can tackle this problem. In the end of Chapter 1, the reader should be sure to see the motivation for the study, the specific knowledge gap (that is, the absence of reliable methodology in calculating SET reaction barriers), and ultimately the research that this research is designed to address.

Chapter 2: Literature Review –It will review previous experimental and computational publications on photoredox catalysis. For instance, recent reviews (and some of them by Prier et al. (2013), Koike and Akita (2015), Twilton et al. (2017)) have documented various organic transformations which can be performed by Ru/Ir photoredox catalysts. In this chapter we will describe how these catalysts work and the reasons that it is important to control the SET step to achieve successful reactions. It will then address major
computational contributions like Demissie et al. (2015), showing DFT's capability to reproduce redox potentials and elucidate mechanisms; Medina and Pinter (2020), that protocols for precise structures and redox properties of Ru complexes are set up; and Gomes and Lopez (2025), that a wide benchmarking of functionals for photoredox redox potentials has been carried out. The review will highlight that although DFT has addressed thermodynamics (redox potentials) effectively, the prediction of kinetic parameters (activation barriers) underlies the DFT approach and represents a neglected area. General studies (e.g. Sperger et al. 2015) warn that the selection of functional can drastically influence barrier heights so the community is encouraged to proceed beyond simple solutions such as B3LYP. Such a literature review would further justify the rationale for our work, for it would highlight the need for systematic comparison of DFT systems concerning the barrier characteristics of photoredox reactions and support goals of the thesis.

Chapter 3: Theoretical Background and Computational Methods – First we shall go over the basic concepts of exchange–correlation functionals, and why such a choice is

critical to have reasonable energetics. The text will address the specific DFT functionals under study, along several rungs of Jacob's ladder — the GGA hybrid B3LYP (Becke's three- parameter exchange with Lee–Yang–Parr correlation); the hybrid PBE0 functional; Minnesota meta-hybrids M06 and M06-2X (for better thermochemistry and kinetics); the long-range-corrected hybrid ωB97X-D (empirical dispersion); and the B2PLYP double- hybrid functional introduced by Grimme. Important references will be referred for the evolution of each functional (e.g. Zhao and Truhlar 2008 in respect of the M06, Chai and Head-Gordon 2008 for the ωB97X-D, Grimme 2006 for the B2PLYP, and so on) and their anticipated behaviour characteristics. Finally, the following important computational elements will be discussed in Chapter 3: the basis sets (e.g., using triple zeta quality basis sets like def2-TZVP for main group components, def2-TZVPP (with Stuttgart-Dresden ECP) for Ir/Ru), the dispersion corrections (Grimme's D3 for functionals that lack it), and implicit solvation models using PCM or SMD for polar solvents, such as acetonitrile, which is designed to simulate the reaction environment. The chapter will delineate the overall computational protocol for the DFT potential energy surface: initial geometry optimizations (for reactants, products and transition states) followed by frequency calculations to obtain activation free energies. Then the program will proceed with the implementation of higher level single-point operations (such as DLPNO-CCSD(T) or CASPT2) for optimized transition states in order to test their efficiency. By elaborating on this theoretical and methodological exposition, Chapter 3 forms the framework and tools with which the research questions areto be handled.

Chapter 4: Benchmarking DFT on Reductive Quenching Reactions –Particularly in this chapter, we consider the outer-sphere reduction of an alkyl halide by an excited Ir or Ru photocatalyst, an illustration of the formation of carbon-centered radicals that result from electron transfer. A proof of concept is the reductive cleavage of benzylic carbon–bromine bonds (e.g. benzyl bromide, $PhCH_2$–Br by photoexcited $[Ru(bpy)_3]^{2+}$ or fac-$Ir(ppy)_3$). Such photocatalysts have been experimentally proved to be effective radical alkyl halide reducers, so the concept is fairly relevant as to a benchmark. Finally, the transition state for the concerted electron transfer and dissociation of the C–Br bond will

be described, including its geometry, and the extent of charge transfer to the TS. The activation free energies corresponding to each DFT functional (B3LYP, PBE0, M06, M06-2X, ωB97X-D, B2PLYP) will be presented and compared. Results will be compared, highlighting the deviation between the ideal barrier heights for each functional, showing H1 (predictable difference) in practice. Where relevant, comparisons with the experimental kinetics (e.g. relative reactivity or estimated activation barriers) or to high-level calculations (CCSD(T) single-point energies) will be used to assess accuracy. The discussion will expose trends — for example, do functionals with greater exact exchange (such as ωB97X-D or M06-2X) predict higher/lower barriers relative to B3LYP and how incorporating dispersion and a suitable basis set impacts the results. As for any strange results (for instance, one functional cannot locate the correct TS or provides an outlier barrier), all will be noted. At the conclusion of Chapter 4, the thesis will have prepared a baseline understanding of functional performance, for a prototypical reductive SET reaction.

Chapter 5: DFT Benchmarking on Oxidative Quenching Reactions- In this chapter, as an analysis of a single case study we will focus on the oxidation of an amine by an excited photocatalyst, a common example in photoredox cycles with sacrificial donors. The model reaction will consist of the one-electron oxidation of a tertiary amine (e.g., triethylamine
(TEA)) by $[Ru(bpy)_3]^{2+}$ or $Ir(ppy)_3$, yielding TEA˙^+ amine radical cation and a reduced metal complex. In many experiments these fast oxidative quench are (often) extremely diffusion-controlled for strongly reducing excited states, while when the driving force is very moderate, a finite activation barrier may emerge because of considerations of Marcus theory. The chapter will describe DFT calculations to locate the crossing point or transition state on the excited-state or ground-state surface corresponding to this outer-sphere electron transfer. I will introduce the expected barrier each function faces for forming the amine radical cation. The findings will test H2, the hypothesis that functionals with the ability to deal with radical cationic species (such as M06 or ωB97X-D) produce more robust barriers. Particular emphasis will be placed on solvent-induced alterations of this process (testing H4): a comparison of SMD with versus without modelled models may be applied to reveal the stabilizing impact of the polar medium on

the charged transition state. The subsequent fast deprotonation of the amine radical cation (though not the main interest, it provides background information for the overall reaction profile) will be discussed in the subsequent chapter. Chapter 5 will evaluate which of the DFT based approaches most closely represent the kinetics of the oxidative electron transfer steps by cross-checking functional performance by comparing with known experimental trends (e.g., catalysts or conditions will quench faster) or with higher-level benchmarks.

Chapter 6: Benchmarking DFT on Decarboxylation and Comparative Analysis: In thischapter a third model photoredox reaction will be examined i.e. photoinduced decarboxylation which is the oxidation of carboxylate to produce CO_2 and produce a radical.

In the traditional example, there may be an excited Ir(III) catalyst like $[Ir(ppy)_2(dtbbpy)]^+$ oxidizing a carboxylate anion (e.g. a benzoate, RCO_2^-), which results in CO_2 extrusion and carbon-centered radical. Decarboxylative photoredox couplings are of important synthetic significance, and can even generate radical species from cheap carboxylic acids. In Chapter 6, we will look at the DFT-calculated barriers for cleavage of the CO_2 bond after transfer of electrons. By contrast, here the electron-transfer to the catalyst forms a short-lived carboxylate radical, which remains for a time until the reaction begins to break. The calculations should most probably address the CO_2 extrusion barrier to the ground state after SET (as in the case of the ET produced a neutral radical which quickly splinters). The performance characteristics will be contrasted over the functionals, to determine if the findings are corroborated in chapter four and five for the third test. Additionally, in Chapter 6 the authors will present an overall comparison among all three reaction types. It will then take the entire dataset to determine if one or two functionals are consistently reliable (to address H5), i.e. do the double-hybrid B2PLYP with a triple-zeta basis in fact outperform in any case, or does the range-separated ωB97X-D give almost same level of accuracy in virtually similar cost? This chapter will review these benchmarking results as a whole, possibly including statistical data (mean unsigned errors using sample reference data, correlation plots regarding DFT vs. reference barriers) to formally rank functionals quantitatively. The

effect of the choice of basis set and dispersion (H3) will be returned to present the results on the smaller basis sets or not controlled for dispersion correction in order to show this effect. By the end of Chapter 6, it is hoped that readers will be able to make out how each tested functional perform in each of these different photoredox barrier predictions and which computational protocol best compromises for accuracy versus power for these systems.

Chapter 7 Conclusions and The Future – The last chapter will present an integrated study of the results and discuss the implications of the benchmarking work for photoredox catalysis studies. It will discuss whether or not the original hypotheses (H1–H5) were supported by the results. For example, the thesis will conclude that a specific DFT functional (or functionals) should be established for determination of single-electron transfer reaction barriers in Ir/Ru photoredox systems which is consistent with experimental or high-level reference data. So, given that ωB97X-D/def2-TZVP with SMD solvation should reproduce benchmark barriers in a few kcal/mol, it might be a popular approach (as hypothesized). It is only a little bit beyond the research horizon. Otherwise, should only a more computational intensive approach (i.e. a double-hybrid on top of a meta-GGA geometry that attains "chemical accuracy") be made, that would then become an aspect of what is likely a best practice to be considered. The chapter will further highlight the scientific observations extracted: e.g., the magnitude of typical SET barriers for these catalysts (determined whether these steps truly pass through as fast and barrier-free or with measurable activation energies) and how the quantum of electronic or solvent effect modulates these barriers. Lastly, a future perspective is given. Results of the study will be put into a wider frame of reference in computational photochemistry - as an ideal application for how the newly validated DFT protocol could be relevant in the context of finding new kinds of photocatalysts (e.g. Fe- or Cu-based systems) for greener catalysis, and be coupled with machine-learning models for more rapid designing of photocatalysts. Next steps, including excited-state surface crossings, or time-dependent DFT for excited-state energetics, will also be described. Chapter 7 will accordingly conclude the thesis highlighting the contribution of the benchmarking study to fundamental knowledge and practical approaches in photoredox catalysis, and

providing indications for future research directions which build on this work.

Hypothesis

The research proposal was proposed based on several main hypotheses (H1–H5), which are expected to be followed in this study due to the anticipated performance of individual DFT functionals and computing conditions on photoredox reaction barriers:

H1: Barriers Functional Performance

Clearly differ by DFT functional type – Different functionals will create radically dissimilar activation barriers per photoredox reaction. We expect that hybrid functionals with modern hybrid characteristics with increased Hartree–Fock exchange (e.g., PBE0, M06-2X, ωB97X-D) or double-hybrid character (i.e., B2PLYP) will increase the barrier level prediction when comparing with semi-local GGAs or hybrid forms with HF content of lower amounts, such as B3LYP. The theory that advanced functionals should reproduce the partial charge-transfer nature of the SET transition states and B3LYP might well underestimate obstacles due to self- interaction error.

• H2: Triplet and Radical States Call for Specialized Functionals - Photoredox catalysis is characterized by triplet excited states and radical intermediates, and thus, we hypothesize that functionals well-known for radical thermochemistry and kinetics (e.g. the M06 family or ωB97X-D) will perform much better than others for calculating photoredox reaction barriers. For instance, the long-range-corrected
ωB97X-D allows reduction of self-interaction errors for one-electron transfer and more reliably produces the barriers to outer-sphere SET processes.

• H3: Basis Set and Dispersion Effects are Non-Negligible – We postulate that we will have to use a high-quality basis set to account dispersion forces for quantitative accuracy in barrier heights. As a matter of practicality a triple-zeta basis (e.g., def2- TZVP or 6-311++G(d,p)) with polarization and diffuse functions is supposed to define a better

picture of the charge distribution in the transition state than a double-zeta basis would. Similarly, such empirical dispersion (Grimme's D3) is expected to make the description of any π-stacking or noncovalent interactions in the catalyst–substrate complex better, especially for functionals such as B3LYP/PBE0 that do not have dispersion corrections by default.

• H4: Effects of Solvation Models on Activation Free Energies: Photoredox reactions typically happen in polar solvents (e.g. acetonitrile) and, we hypothesize, having a solvation model implicitly in the framework will substantially reduce the calculated activation free energies in the mechanism on charged species. A continuum solvent model (PCM or SMD) should stabilize the ionic intermediates as well as the transition states (oxidized photocatalyst or substrate radical cation). Consequently these will significantly lower barriers for comparison than in gas-phase calculations. We hypothesize that gas-phase DFT may overestimate barrier heights, whilst solvent inclusion will bring determined number closer to experimental reality.

• H5: A Best-Performing Functional Set of Functionals emerge: We anticipate that one or two DFT functionals should give activation barriers consistent with reference data of optimal agreement, hence it will be an outlier among the proposed systems. We expect for example that the double-hybrid B2PLYP will be a top performer (along with the triple-zeta basis and the dispersion correction), as it has shown to perform well across a wide range of thermochemical benchmarks. Finally, the
range-separated hybrid ωB97X-D might well be the best compromise between accuracy and computational cost. Figuring this efficient functional or approach out represents one of the main objectives of the project, ultimately informing future work on photoredox kinetics.

c) Methodology

Total Research Approach: A systematic computational benchmarking strategy will be used in this research. Activation free energies for selected photoredox reactions will be calculated with several DFT functionals and compared to each other and to higher-level or experimental reference values. All calculations will be made in a consistent way, so that variations in outcome are accounted for by the selection of functional (and other

variables of interest) instead of inconsistent modeling assumptions. The following outlines the main details regarding the specifics of the methodology, namely selection of DFT functionals, model systems (catalysts and reactions) and computational settings.

DFT Functionals and Computational Settings: We wish to assess 6 typical DFT functionals covering a broad range of functional types. These consist of: B3LYP (a classical hybrid GGA), PBE0 (a non-empirical hybrid GGA), M06 and M06-2X (Minnesota meta-hybrid functionals designed for thermochemistry and kinetics), ωB97X-D (a long-range-corrected hybrid GGA with empirical dispersion) and B2PLYP (a double-hybrid functional incorporating perturbative second-order correlation). From this diverse set, ranging from semi-local hybrids up to a double hybrid, we will explore how the functional choice affects the anticipated reaction barriers. All DFT calculations will use a triple-zeta quality basis set to have adequate accuracy in electron distributions. Specifically, we will use basis sets such as def2-TZVP (C, H, N, O, etc.) and a core potential basis (e.g., def2-TZVPP with Stuttgart- Dresden ECP) for heavy metals Ir and Ru. This is consistent with our H3 hypothesis that a high-quality basis is necessary for reliable barriers. To capture dispersion forces (π–π stacking, van der Waals interactions, etc.) in precursor complexes, Grimme's D3 dispersion correction will be included for functionals that do not inherently account for dispersion.

Implicit solvation will be applied using the SMD continuum model (which specifies an organic polar solvent such as acetonitrile or dichloromethane) to mimic typical experimental conditions. Due to the presence of charged open-shell species that require careful electronic convergence, all calculations will be carried out using tight self-consistent field (SCF) convergence criteria and fine geometry optimization thresholds. It is a robust computational protocol that aims to achieve the trade-off between precision and feasibility, and one part of the goal of the study is to verify that these approaches (triple-zeta basis, D3, SMD solvation) are indeed required to get dependable results (according to H3 and H4).

Selection of Photocatalysts: Five well-known Ir(III) and Ru(II) photoredox complexes from well-studied systems representing the scope of common systems found in literature have been chosen as the 5 test photocatalysts:

• $[Ru(bpy)_3]^{2+}$ – Tris(2,2′-bipyridyl)ruthenium(II), the archetypal Ru-based photoredox catalyst with well-known photophysical and redox properties and provides the standard Ru-based photoredox catalyst. It possesses a moderately strong excited-state oxidizing power with a long-lived triplet metal-to-ligand charge transfer (MLCT) state (lifetime $\sim 1\,\mu s$) and is considered a useful benchmark for visible-light photocatalysis.

• fac-$Ir(ppy)_3$ – Facial tris(2-phenylpyridine)iridium(III), a homoleptic Ir catalyst with excellent reducing power within the excited state. Ir(ppy)_3 may, for instance, readily donate an electron to substrate species, such as alkyl halides, and is significant for reductivephotoredox cycles.

• $[Ir(ppy)_2(dtbbpy)]^+$ – A heteroleptic Ir(III) complex with two ppy ligands and one di-tert- butyl-2,2′-bipyridine (dtbbpy) ligand. The redox profile of this photocatalyst is somewhat different from Ir(ppy)_3—it possesses an electron-rich diimine (dtbbpy), making it a robust ground-state oxidant, often being employed to power more demanding oxidative photoredox reactions.

• $[Ir(dF(CF_3)ppy)_2(bpy)]^+$ – A highly reducing Iridium photocatalyst using fluorinated ligands. Here $dF(CF_3)ppy$ is 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, a strongly electron-withdrawing form of ppy. In this case, the addition of F and CF_3 groups dramatically increases the excited-state reducing power, which results in activation of veryinert bonds (good for difficult reductive quenching conditions).

• $[Ru(phen)_3]^{2+}$ (or $[Ru(bpy)_2(phen)]^{2+}$) – A variant of the Ru polypyridyl family where phen = 1,10-phenanthroline. Incorporating a phenanthroline-based complex enables us to examine the effect of subtle changes to a ligand in Ru(II) on computed barriers. $Ru(phen)_3^{2+}$ has excited-state properties akin to $Ru(bpy)_3^{2+}$, with the different ligand electronics having been shown to influence reaction energetics, which will be examined to test the general character of the conclusions generated from the bpy-based systems. Through the comparative observations of the Iridium and Ruthenium complexes, homoleptic and heteroleptic forms and catalysts with various redox potentials, we guarantee extensive applicability of our benchmarking findings to Ir/Ru photoredox systems.

Selection of Model Reactions: In addition to the catalysts we selected three prototypical single-electron transfer reactions, encompassing the main mechanistic pathways of photoredox catalysis. There is a radical intermediate formed by initial outer-sphere electron transfer of the excited photocatalyst (PC⋆) with an organic substrate from each reaction.

The chosen reactions are:

Reductive Quenching (Alkyl Halide Reduction) – Reduction of an alkyl halide (e.g. benzyl bromide, $PhCH_2–Br$) by the excited photocatalyst. Here, PC* acts as an electron donor to the substrate and cleaves the C–Br bond to create a benzyl radical and Br^- (the catalyst becomes oxidized, PC^+). This mimics the reductive quenching cycle that is essential in photoredox catalysis, in which a photocatalyst transfers an electron to a substrate (frequently a halide) that promotes radical synthesis.

1. Oxidative Quenching (Amine Oxidation) – Oxidation of tertiary amines (e.g., triethylamine, NEt_3) by excited photocatalyst. PC accepts an electron from the amine, which forms the amine radical cation* ($R_3N^+•$) and the reduced version of the photocatalyst, PC^-. This is the oxidative quenching pathway where the excited catalyst is reduced by a sacrificial donor. Tertiary amines such as NEt_3 or DIPEA are frequently used as sacrificial reductants when using photoredox systems and we wish to identify the barrier for their one-electron oxidation for monitoring the efficiency of catalyst turnover.

2. Decarboxylative SET (Carboxylate to Radical) – The oxidation of a carboxylate anion (e.g. benzoate, $PhCO_2^-$) by a strongly oxidizing excited catalyst, leading to CO_2 extrusion and formation of a radical. This mimics photoredox decarboxylation reactions, in which an aromatic or aliphatic carboxylate oxidizes one electron, losing CO_2 while giving a carbon- centered radical. These steps are crucial for coupling reactions that utilize carboxylic acids as radical precursors. This mechanism leads to a radical $[RCO_2]•$ transition followed by rapid fragmentation into CO_2 + R• (initial electron transfer). Next step is to find the barrier that comes with the $C–CO_2$ bond-breaking after ET, which is more or less a radical fragmentation of the neutral (or singly oxidized) potential surface.

The studies of each reaction will be carried out with respect to the different photocatalysts in mind. The benzyl bromide reduction will, for instance, be modeled with a Ru-based and an Ir-based photocatalyst to see how the barrier may vary, whilst the amine oxidation and decarboxylation might be studied with a couple of the catalysts (particularly those most relevant: e.g. oxidative quenching with $Ru(bpy)_3^{2+}$ and $Ir(ppy)_3$, decarboxylation with a very strong oxidant like $Ir(dF(CF_3)ppy)_2(bpy)^+$). This yields a matrix of catalyst–substrate pairs which are used to calculate activation barriers, making sure that we will sample bothreductive and oxidative forms of photoredox catalysis.

Computational Method: For each selected catalyst–reaction set-up, the following calculations will be conducted: (1) Optimize the ground-state geometry for the reactants, products, and when possible the encounter complex of the catalyst and substrate (singlet ground state for closed-shell species or the case-specific open-shell state). (2) Excited-state considerations: In the photochemical step, the catalyst is in its long-lived lowest excited state (usually triplet MLCT for Ir/Ru complexes). Then, we start the electron-transfer calculation from the excited-state of the photocatalyst. We can actually try to get here by using the ground state potential energy surface in the combined system but putting the catalyst in a spin-state that is equivalent to that of triplets (the entire system would again be treated as doublet owing to one unpaired electron after ET). (3) Transition State Search: We will search for transition states (TS) corresponding to the electron transfer in relation to a bond cleavage/formation. Where electron transfers are primarily on the outer sphere, it may be difficult to find a TS since the interaction process may be barrierless or the barrier may be very shallow. In such scenarios, we will be guided by methods such as constrained DFT scans or employing Marcus theory to compute the activation barrier from thermodynamic parameters (reorganization energies and driving force). TS should be reached for the concerted processes like breaking C–Br bond with ET by stretching the bond and letting an electron transfer. (4) Frequency analysis: Each TS where found will be checked by vibrational frequency analysis to say that it has to have only a single imaginary frequency around the electron-transfer/bond-breaking coordinate and to calculate the zero-point energy and thermal corrections for the activation free energy (ΔG^‡). (5) Energy Refinement at Single-Point Level: When feasible, we will use higher-level calculations of single points on critical points

(especially TS geometries). In smaller models (e.g. truncated ligand models, if appropriate), DLPNO-CCSD(T) or multi-configurational approaches such as CASPT2 will be employed to calculate a best-estimate of the barrier. These will now be considered as reference values to compare the DFT outputs (supports hypothesis H5's aim of how close the DFT is to the reference). (6) Comparison and analysis: The activation free energies of all functionals will be collected. Data will be examined by comparison with reference (computational or experimental) data for its statistical properties and other data. We will compute values for numbers of functional numbers such as the mean unsigned error and maximum deviation (relative to reference). We will also investigate potential interrelationships between functionals (e.g. comparing the value for block lines drawn between B3LYP predicted and ωB97X-D predicted) (e.g. determining whether there is a systematic offset or random scatter). The ideal functional would have slope ~1 correlation with high-level data and negligible scatter (small error). Using these analyses, we anticipate observing distinct patterns and giving recommendations. The approach is intentionally designed to be exhaustive and internally consistent. If, like you were saying, you do end up applying multiple functionals to the same set of well defined reactions and catalysts, we will have a fair head-to-head comparison. The addition of different functionals will help to test our hypotheses H1 and H2 regarding functional performance; provide the reliability of a strong basis set and solvation tests H3 and H4; and compare with reference data to test the hypothesis H5 and find out the highest performing strategy. The result will be a well established computational protocol concerning barriers for photoredox reactions and quantified uncertainties. This is a computational study, so it depends on the computing resources available rather than the experimental logistics to be capable of using this protocol. All the DFT calculations needed are moderate in cost (ranging from hours for a single point through to a few days for sophisticated TS optimizations on cluster computers), and the more expensive DLPNO-CCSD(T) validations will be restricted to as small a subset of cases as possible to allow for the remaining tractability of the project. Previous literature (e.g. Lopez 2025 benchmark of 147 functional/basis combinations) demonstrates that even larger computational surveys are feasible; the focused study on fewer systems is definitely within reach. Overall the methodology lays

the groundwork for us to accomplish the research goals as we can confidently evaluate "What are competing DFT functionals for predicting photoredox reaction barriers, and which configuration gives the most accurate results?".

Software Requirements: In order to successfully serve the computational goals of this research, dedicated quantum-chemical software packages shall be necessary. All density functional theory (DFT) calculations as well as geometry optimizations, transition-state searches, solvation-model computations, excited-state analyses, etc. are performed with software packages including Gaussian 16 / Gaussian 09, ORCA, and Q-Chem. The building of the structures and vibrational mode examination will be done using GaussView. To be done, data processing, statistical analysis and generation of energy-comparison plots will be performed in Python with scientific libraries including NumPy, Matplotlib, and Pandas.
Implementing these software tools is essential for accurate and reliable computational benchmarking, with reproducible methods to ensure that the study is always done correctlyand with confidence.

Catalyst Designing:

In photoredox catalysis with Iridium and Ruthenium complexes, computational methods – especially DFT simulations guided by benchmarking – are invaluable for rational catalyst design and mechanistic insight. The critical single-electron transfer (SET) step often dictates reaction kinetics and selectivity, so accurate prediction of its activation free energy is pivotal to explain why certain photoredox reactions succeed and to guide new catalyst designs. Because direct experimental measurement of such transient radical barriers is rare, DFT provides an accessible way to estimate these energetics. However, modeling outer-sphere SET barriers pushes DFT to its limits: these systems involve open-shell radicals, charged species, heavy metal centers, and strong solvent effects. Different DFT functionals often yield widely varying barrier heights; for instance, the popular B3LYP functional tends to underestimate barriers due to self-interaction error. Thus, benchmarking various functionals (B3LYP vs modern hybrids like M06 or long-range ωB97X-D, etc.) against experimental or high-level data is essential to identify

which methods best capture the partial charge-transfer character of the SET transition state. Long- range-corrected and high-exchange functionals generally predict higher, more realistic barriers than semi-local hybrids, owing to better handling of radical charge distribution; indeed, functionals known for radical and kinetic accuracy (e.g. M06 family or ωB97X-D) outperform simpler functionals in photoredox contexts. Such DFT benchmarking yields an optimized protocol – for example, ωB97X-D with a triple-ζ basis and SMD solvation reproduces benchmark SET barriers within a few kcal/mol. Importantly, including a polar solvent model (e.g. SMD) is crucial: solvation stabilizes charged intermediates and transition states, significantly lowering computed barriers (gas-phase calculations overestimate them). With a validated DFT methodology in hand, researchers can then screen and refine catalyst structures in silico: for example, varying ligand frameworks or metal centers allows prediction of changes in redox potentials and barrier heights before synthesis, pinpointing modifications that yield lower activation energies and improved selectivity in the catalytic cycle. This approach also enables tuning of a photocatalyst's redox properties to ensure its excited-state oxidizing/reducing power is optimal for the target reaction, and it facilitates the search for cost-effective alternatives to Ir/Ru. Notably, computational screening can reveal earth-abundant candidates (e.g. Fe or Cu polypyridyl complexes) with suitable electronic characteristics to replace expensive Ir/Ru catalysts. In summary, by leveraging DFT-predicted reaction barriers and rigorous solvation modeling, chemists can rationally guide the design of new photoredox catalysts with enhanced selectivity, optimized redox properties, and greener, lower-cost profiles.

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